

# Studies on the Sorption and Permeation of Acid dyes through Silk fibroin Membrane(Ⅲ)

—Permeation of Acid dyes through the Silk fibroin Membrane—

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견 피브로인 막을 통한 산성염료의 흡착과 투과에 관한 연구(Ⅲ)

—견 피브로인 막을 통한 산성염료의 투과—

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## 적 요

견 피브로인 막을 통한 투과실험으로, 종전의 전섬유로는 얻을 수 없었던 투과 및 확산거동에 대하여, Dual mechanism을 적용하여 고찰하였으며, 아울러 염료의 구조가 이러한 물리화학적 성질에 미치는 영향에 관해서 고찰한 결과를 요약하면 다음과 같다.

- 1) 전체적인 확산계수  $D_{(c)}$ 는 주로 Langmuir-type 확산계수  $D_L$ 에 의해서 결정된다.
- 2) 농도에 따른 확산계수의 조사에서 Dye I (monobasic dye)에서는 뚜렷한 최대치가 관찰되었으나, Dye Ⅲ (trisulfonic acid dye)에서  $D_p$ 는 거의 의미가 없는 것으로 나타났다.
- 3) 견 피브로인에 있어서 산성염료의 확산은 sulfonic acid group의 도입에 따라 점점 느리게 되고,  $D_L$ 은 온도의 증가에 따라 더 큰 값을 나타냈다.
- 4) 염료 음이온의 하전수가 클수록 확산계수는 chemical potential gradient model에 더욱 더 가깝게 된다.
- 5) 투과의 활성화 에너지는 sulfonic acid group의 도입에 따라 감소되었다.

## I. Introduction

The information on the diffusion behaviour is very important for dyeing process. The transient diffusion profiles, i.e., the dye distribution curve in the polymer matrix at different penetration times, as determined by film-roll method are very informative for the kinetic analysis of this system. However, the method has its own problems, such as the limited number of layers in a film roll and the presence of water layers between the successive film layers. The

need for a film of relatively large size is an additional drawback as compared with the steady-state permeation method. The latter approach is simpler and does not need any special technique in the performances of the experimental.

It was suggested that the sorption and diffusion of acid dyes in over dyeing systems could be quantitatively analyzed by the dual sorption and diffusion models, which were based on the two distinct Langmuirean and Nernstean species (Fack & Eollinger, 1959; Nango et al., 1974; Komiyama et al., 1977). Diffusion of acids, especially dye acids, in

nylon has been widely investigated and the results have been summarized by Peters (Peters, 1975).

In contrast to these studies on strong acids, the sorption and diffusion of simple weak acids by polyamide has been fully investigated by Iijima et al. (1980). It was pointed out that strong acids, such as hydrochloric acid and trifluoroacetic acid, are sorbed only by Langmuir type and acetic acid which is the weakest acid among the acids used, shows the greatest contribution of partition type sorption. And the results for the diffusion coefficient have shown that the contribution of partition species in a total flux is dominant in the case of the acetic acid.

On the other hand, McGregor et al. (1962) have suggested the bimodel diffusion of dye in nylon, namely the dye adsorptions on the charged amino groups and the amide groups in nylon. Hopper et al. (1970). have assumed that the diffusion of acid dyes in nylon is described in terms of the electrochemical potentials of the dyes rather than adsorption model.

In this study, an attempt has been made to obtain more detailed information for the dual mechanism by means of the steady-state permeation measurement. In addition, the information for the diffusion of acid dyes in silk fibroin was investigated.

## II, Experimental

### 1. Materials

The silk fibroin membrane used in this work was (Bae and Tak, 1989a, 1989b) The membrane thickness measured by means of thickness gauge (Han Won Co.) with a precision of  $\pm 1\mu\text{m}$ , was about  $31\mu\text{m}$ . The acid dyes used were Orange II (Dye I), Sunset Yellow (Dye II) and sulfanilic acid 2-naphthol-3,6-disulfonic acid (R acid) (Dye III). The preparation and purification of these dyes have been described previously. (Bae and Tak, 1986b)

### 2. Determination of the permeability coefficients

To determine the permeability coefficients of the dye anions through the silk fibroin membrane, the steady-state method was used. The cell used consists of two compartments, A and B, whose volumes are

250ml and 50ml, respectively (see Fig. 1). The dye concentration in cell A was kept in the range of  $10^{-5}$  to  $10^{-4}$  mol/l with pH 2 adjusted by adding hydrochloric acid. The silk fibroin membrane was placed between the two compartments with teflon seals. And the solutions in A and B were stirred as efficiently as possible. During the experiment, the dye molecules in A permeate into B through the membrane. Aliquots of dye solution were taken out of cell B at appropriate time intervals and the dye concentration was determined spectrophotometrically. Cell B was refilled each time with equal amounts of blank hydrochloric acid solution. As the constancy of the concentration in cell A throughout the experiment was a fundamental necessity, the volume of the solution A was designed to be sufficiently large to ensure the infinite bath conditions in the case of dilute solutions. The permeation apparatus shown

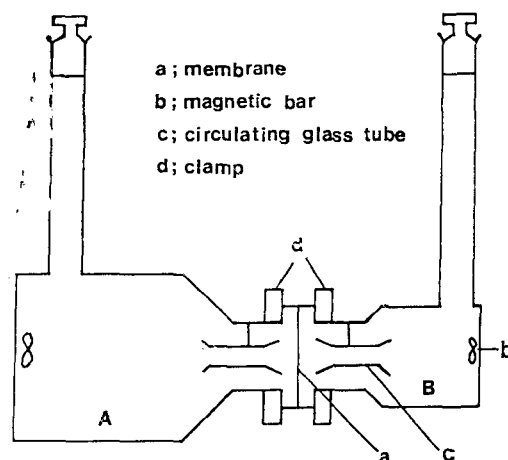


Fig. 1. Permeation Cell.

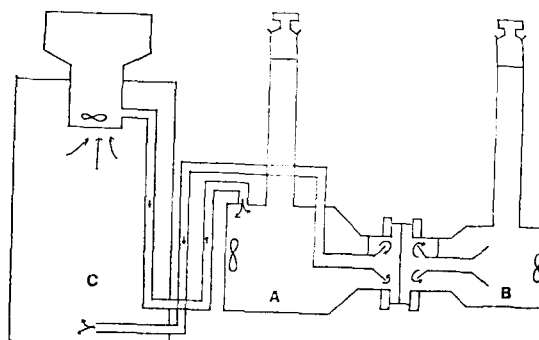


Fig. 2. Modified permeation Cell.

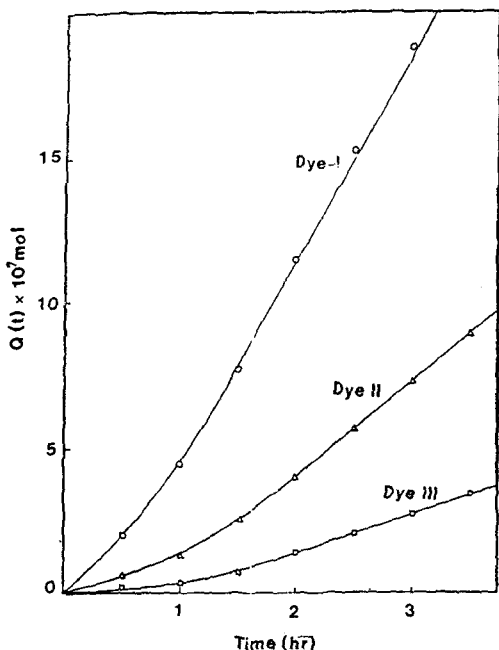


Fig. 3. Permeation of different dyes through silk membranes.

- Dye I : Concentration;  $1.11 \times 10^{-5}$  mol/l,  
 membrane thickness;  $29 \mu\text{m}$ ,  $50^\circ\text{C}$ .  
 Dye II : Concentration;  $1.26 \times 10^{-5}$  mol/l,  
 membrane thickness;  $30 \mu\text{m}$ ,  $50^\circ\text{C}$ .  
 Dye III : Concentration;  $1.18 \times 10^{-5}$  mol/l,  
 membrane thickness;  $30 \mu\text{m}$ ,  $50^\circ\text{C}$ .

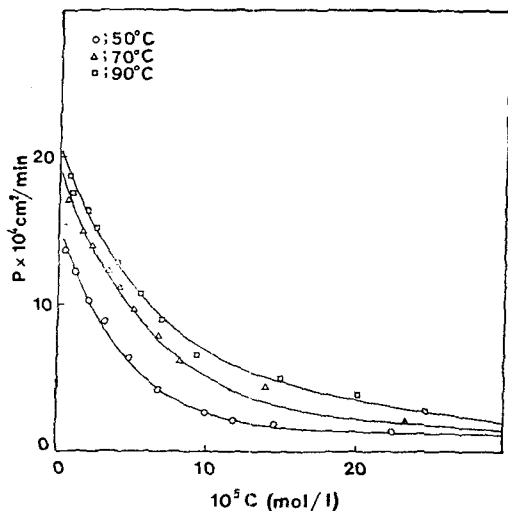


Fig. 4. The permeability coefficients vs. concentration for Dye I through silk membrane at the various temperatures.

in Fig. 2 had the total upstream volume (A+C) of approximately 3,300ml. The agitation of the dye solutions was carried out as efficient as possible to minimize the stagnant boundary solution layers on the surfaces of the membrane.

The examples of the experimental results obtained are shown in Fig. 3. For the steady-state condition, the amount of dye permeated through the membrane against time should give a linear relationship, which gives the permeability coefficient P. The permeability

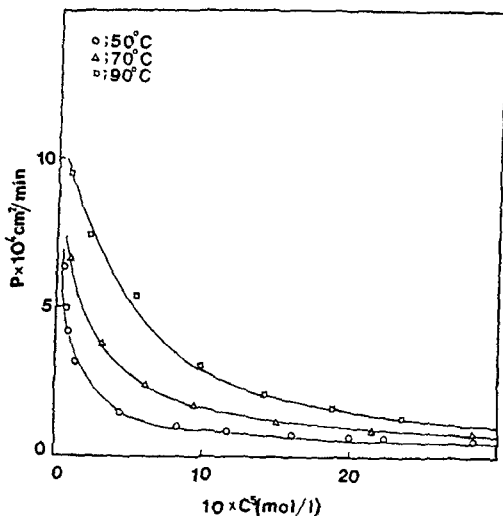


Fig. 5. The permeability coefficients vs. concentration for Dye II through silk membrane at the various temperatures.

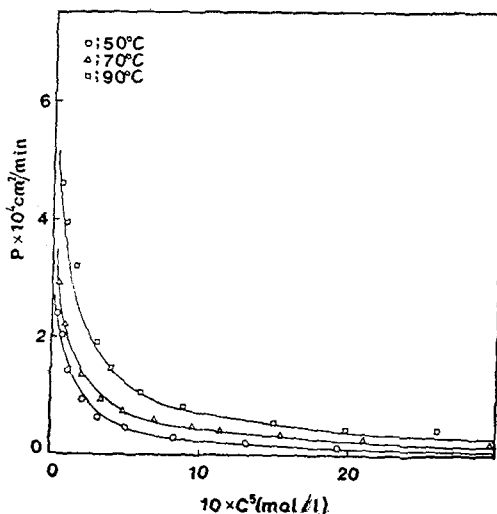


Fig. 6. The permeability coefficients vs. concentration for Dye III through silk membrane at the various temperatures.

coefficients vs. dyebath concentration for each dye in silk fibroin are plotted and shown in Figures 4-6.

### III. Results and Discussion

As described in the preceding works (Bae and Tak, 1989b), the sorption and diffusion of dye can be explained by the dual species. Thus, the sorption and diffusion of dye in the acid dyeing of silk can be described by the following equation,

$$\begin{aligned} C &= C_p + C_L \\ &= K_p C_0 + \frac{K_L S C_0}{z(1+K_L C_0)} \\ &= \frac{\theta}{K(1-\theta)} + \frac{S\theta}{z} \end{aligned} \quad (1)$$

where  $C$  is the dye concentration in silk in equilibrium with the dyebath concentration  $C_0$ ,  $S$  the saturation value,  $z$  the basicity of dye anion,  $K_p$  and  $K_L$  are constants,  $K=K_L/K_p$  and  $\theta=z C_L/S$ .

If the diffusion of an acid dye into silk is controlled by the diffusion coefficient  $D(c)$  with dye concentration, it can be explained in terms of the relation between activity and concentration of the dye anion alone.

The diffusion coefficient  $D(c)$ , defined by Fick's first law, is written as

$$J = -D(c) \partial C / \partial X \quad (2)$$

where  $J$  is the flux of diffusion in a unit time through unit area,  $C$  is the concentration and  $X$  is the distance.

Neglecting the diffusion potential, we assume that dye molecules in the dual states are subject to flow according to the chemical potential gradients, i.e.,

$$\begin{aligned} J &= -\frac{1}{RT} \{ D_L^0 C_L (\partial \mu_L / \partial C) \\ &\quad + D_p^0 C_p (\partial \mu_p / \partial C) \} \frac{\partial C}{\partial X} \end{aligned} \quad (3)$$

where  $J$  is the total flux,  $D_L^0$  and  $D_p^0$  are diffusion coefficients of the respective species,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $\mu_L$  and  $\mu_p$  are chemical potentials of the respective species.

Compared eq.(2) with eq.(3),  $D(c)$  can be rewritten by

$$D(c) = \frac{1}{RT} \{ D_L^0 C_L (\partial \mu_L / \partial C) + D_p^0 C_p (\partial \mu_p / \partial C) \} \quad (4)$$

On the assumption of local equilibrium, the chemical potentials for the dyes in the two states are the same. Thus,  $\partial \mu / \partial C$  can be obtained as

$$\begin{aligned} \partial \mu_L / \partial C &= \partial \mu_p / \partial C \\ &= \frac{RTKz(1-\theta)}{\theta \{ KS(1-\theta)^2 + z \}} \end{aligned} \quad (5)$$

and substituting eq. (5) into eq.(4), then

$$D(c) = \left\{ D_L^0 \frac{\alpha(1-\theta)}{\alpha(1-\theta)^2 + z} + D_p^0 \frac{z}{\alpha(1-\theta)^2 + z} \right\} \quad (6)$$

where  $\alpha=KS$ .

The first ( $D_L$ ) and the second ( $D_p$ ) term in the right hand side of eq.(6) represent the contributions of the respective species to the apparent diffusion coefficients.

On the other hand, assuming that eq.(1) is justified for  $z > 1$  on an empirical basis, (Tak et al., 1979) we expect the following expression for the differential permeability coefficient;

$$P(c) = K_p D_p^0 + \frac{K_L S_L D^0}{z(1+K_L C_0)} \quad (7)$$

This leads to the following expression for the integral permeability coefficient.

$$\bar{P}(c) = K_p D_p^0 + \frac{D_L^0 S}{z(C_{0A} - C_{0B})} \ln \frac{1+K_L C_{0A}}{1+K_L C_{0B}} \quad (8)$$

Where  $C_{0A}$  and  $C_{0B}$  are the dye concentrations in the solution on each side of the membrane, i.e., in half-cell  $A$  and  $B$ , respectively. According to eq. (8), a plot of  $\bar{P}(c)$  against  $\frac{1}{z(C_{0A} - C_{0B})} \ln \frac{1+K_L C_{0A}}{1+K_L C_{0B}}$  should be a straight line with intercept  $K_p D_p^0$  and slope  $S D_L^0 / z$ .

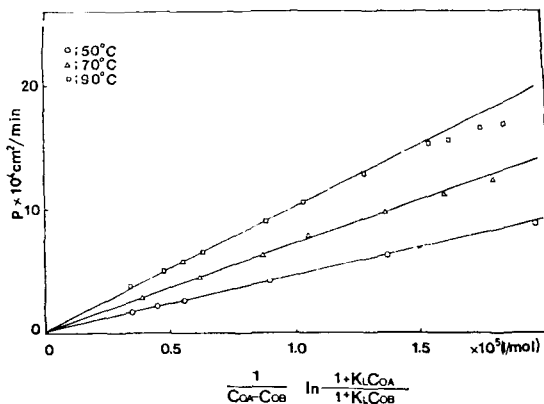


Fig. 7. Linear plots of integral permeability coefficient according to eq. (8) in Dye I at different temperatures.

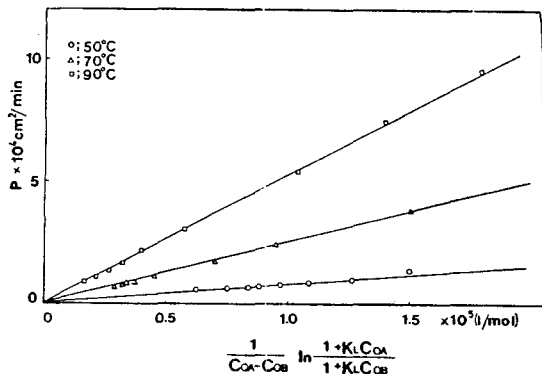


Fig. 8. Linear plots of integral permeability coefficient according to eq. (8) in Dye I at different temperatures.

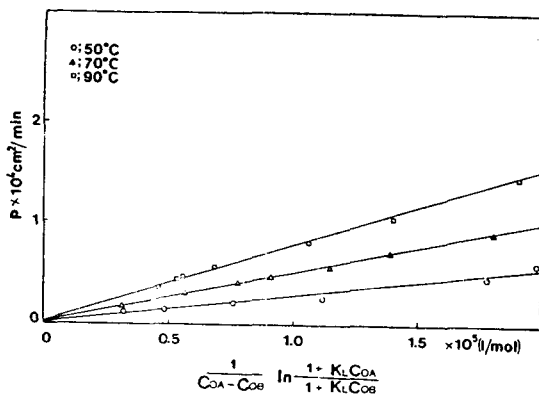


Fig. 9. Linear plots of integral permeability coefficient according to eq. (8) in Dye II at different temperatures.

Plots of the experimental data according to eq. (8) are shown in Figs. 7~9. From the straight lines in these figures  $D_p^0$  and  $D_L^0$  were determined by eq. (8)

with the values of  $K_P$ ,  $K_L$  and  $S$  obtained in the previous work. (Bae and Tak, 1989a, 1989b) The results are summarized in Table 1.

On the other hand, the relationship between the diffusion coefficient and permeation coefficient can be expressed as follows,

$$\begin{aligned} \bar{P} &= SD \\ S &= C/C_0 \end{aligned} \quad (9)$$

where  $\bar{P}$  is permeability coefficient,  $D$  diffusion coefficient,  $S$  solubility parameter, and  $C$  the dye

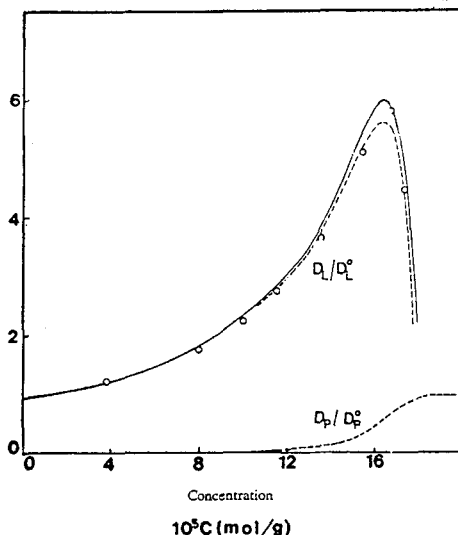


Fig. 10. Concentration dependence of diffusion coefficient of Dye I determined by eq. (9) at 50°C: Solid line refers to calculated  $D$  values which are made up of  $D_L$  and  $D_P$  contributions obtained by the steady-state permeation method. (shown separately by broken lines).

Table 1. The parameters for polybasic acid dye diffusion in silk fibroin.

| Z | Temperature (°C) | $K_P$ (l/g) | $K_L \times 10^{-5}$ (l/mol) | $S \times 10^5$ (eq/g) | $D_0^P \times 10^8$ (cm <sup>2</sup> /min) | $D_0^L \times 10^8$ (cm <sup>2</sup> /min) |
|---|------------------|-------------|------------------------------|------------------------|--------------------------------------------|--------------------------------------------|
| 1 | 50               | 0.380       | 2.73                         | 17.93                  | 2.10                                       | 2.90                                       |
|   | 70               | 0.270       | 2.40                         | 17.85                  | 1.60                                       | 5.30                                       |
|   | 90               | 0.251       | 1.45                         | 17.78                  | 1.90                                       | 8.90                                       |
| 2 | 50               | 0.182       | 5.66                         | 18.52                  | 2.11                                       | 1.08                                       |
|   | 70               | 0.165       | 3.17                         | 18.73                  | 1.88                                       | 3.48                                       |
|   | 90               | 0.143       | 2.10                         | 18.89                  | 3.12                                       | 7.25                                       |
| 3 | 50               | 0.015       | 10.80                        | 22.36                  | 0.88                                       | 0.44                                       |
|   | 70               | 0.011       | 9.49                         | 21.76                  | 0.91                                       | 0.91                                       |
|   | 90               | 0.012       | 7.23                         | 21.78                  | 0.90                                       | 1.67                                       |

concentration in silk at equilibrium with the dyebath concentration  $C_0$ .

The values of  $D_p^0$  and  $D_L^0$  determined by eq.(8) have been used to calculate the lines shown in Figs. 10~18. The broken lines give the relative diffusion coefficients of the respective species. These indicate that the diffusion coefficient increases up to near saturation of the amino groups.

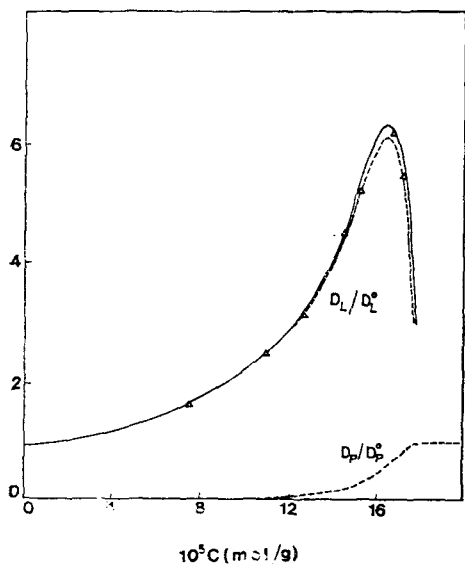


Fig. 11. Concentration dependence of diffusion coefficient of Dye I determined by eq.(9) at 70°C. Meaning of lines as in Fig. 10.

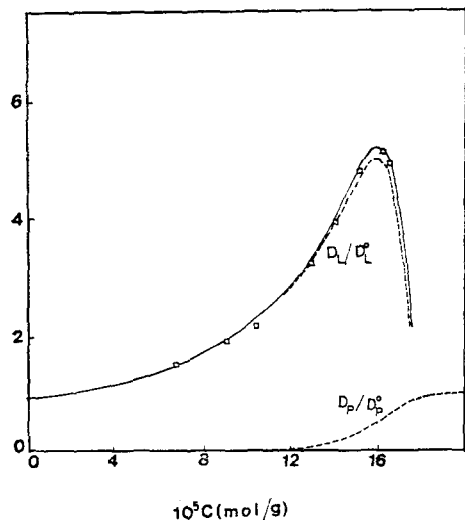


Fig. 12. Concentration dependence of diffusion coefficient of Dye I determined by eq.(9) at 90°C. Meaning of lines as in Fig. 10.

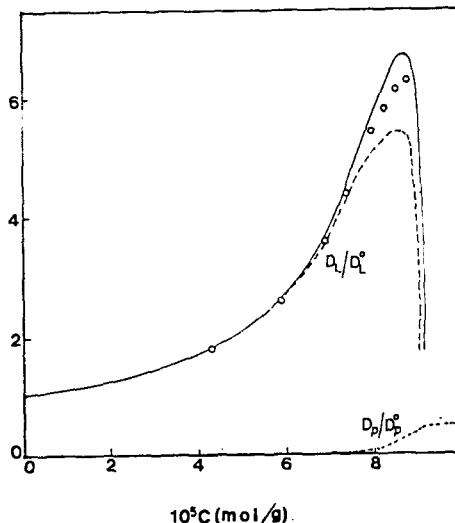


Fig. 13. Concentration dependence of diffusion coefficient of Dye II determined by eq.(9) at 50°C. Meaning of lines as in Fig. 10.

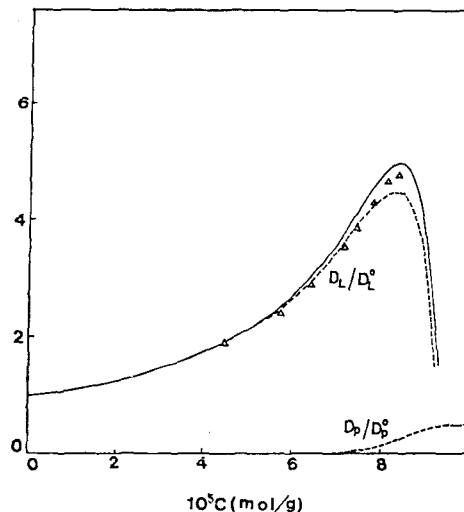


Fig. 14. Concentration dependence of diffusion coefficient of Dye II determined by eq.(9) at 70°C. Meaning of lines as in Fig. 10.

In the case of the monobasic dye (Dye I), a clear maximum is observed at this point. The overall value of  $D$  is largely determined by  $D_L$ , i.e., by the contribution of the  $L$  species, as shown by the pertinent broken line in Figs. 10~12. The solid line, which is the superposition of the  $D_P$  and  $D_L$  contributions, agrees very well with the experimental points. However, it is observed that the difference is not significant with temperature variation.

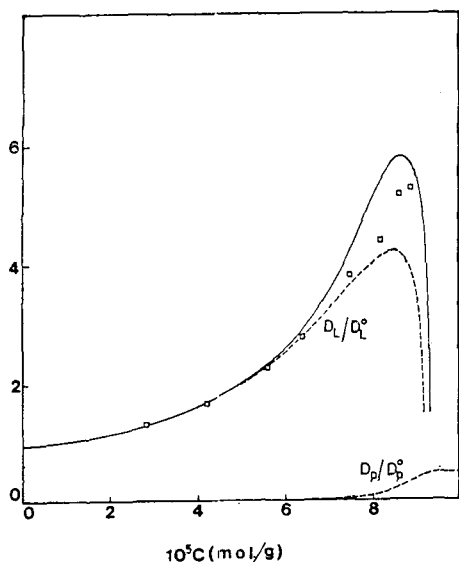


Fig. 15. Concentration dependence of diffusion coefficient of Dye II determined by eq.(9) at 90°C. Meaning of lines as in Fig. 10.

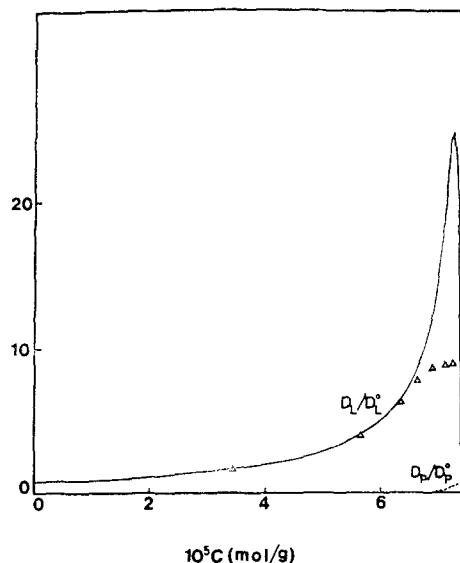


Fig. 17. Concentration dependence of diffusion coefficient of Dye III determined by eq.(9) at 70°C. Meaning of lines as in Fig. 10.

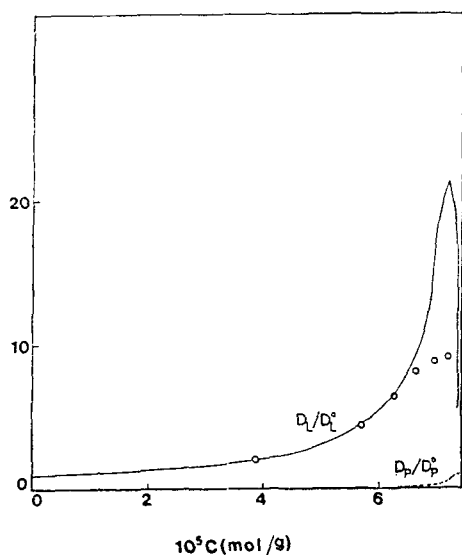


Fig. 16. Concentration dependence of diffusion coefficient of Dye III determined by eq.(9) at 50°C. Meaning of lines as in Fig. 10.

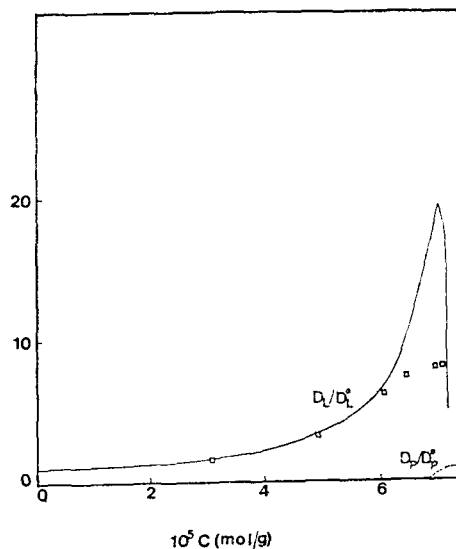


Fig. 18. Concentration dependence of diffusion coefficient of Dye III determined by eq.(9) at 90°C. Meaning of lines as in Fig. 10.

In the case of Dye II (Fig. 14 and 15), the contribution of  $D_P$  is not significant at 70° and 90°C. Some discrepancy between calculated data (solid line) and results obtained by eq.(9) may be recognized above the concentration of  $6 \times 10^{-5}$  mol/g.

In the case of Dye III, the contribution of  $D_P$  is hardly significant. And the results obtained by eq.(9) is lower than that obtained by eq.(6) (solid line) above the concentration of  $6 \times 10^{-5}$  mol/g. Compared with the  $D^0$  values for different dyes in Table 1, it can be said that the diffusion of anionic dyes in silk

fibroin becomes slower with the introduction of sulfonic acid groups. This effect can be considered as the steric and/or electrostatic point of view. Thus, the additional sulfonic acid group may hinder the translation of the dye in the polymer matrix, because of its bulkiness and attractiveness to the positively charged sites ( $-\text{NH}_3^+$ ) in the polymer.

On the other hand,  $D_L^0$  value becomes larger with higher temperature. It can be thought on account of the increase of the activity of dye anion. However, the precise comparison of the  $D_p^0$  values is not very meaningful because of their uncertainties.

On the other hand, the following expressions are well known for the replacement of the concentration gradient in Fick's first law to give the concentration dependence of diffusion coefficient. (Sekido et al., 1965; Peters et al., 19)

$$D(c) = D^0 \frac{1}{(1-\theta)^2} \text{ (activity gradient model) } \quad (10)$$

$$D(c) = D^0 \frac{1}{(1-\theta)} \text{ (chemical potential gradient model) } \quad (11)$$

In eq.(6),  $D_p$  tends to be zero when  $\alpha$  is large enough to give  $\alpha(1-\theta)^2 \gg z$  and hence eq.(6) yields eq.(11).

Figs. 19~21 show the comparison of the results obtained by eq.(9) of mono-, di- and trisulfonic acid dye with the theoretical relationship of eq.(10) and eq.(11). It is clearly observed that the larger the charge number of the dye anion, the nearer the data obtained by eq.(9) with the theoretical curve given by eq.(11). It is suggested that the contribution of partition mode decreases with increasing

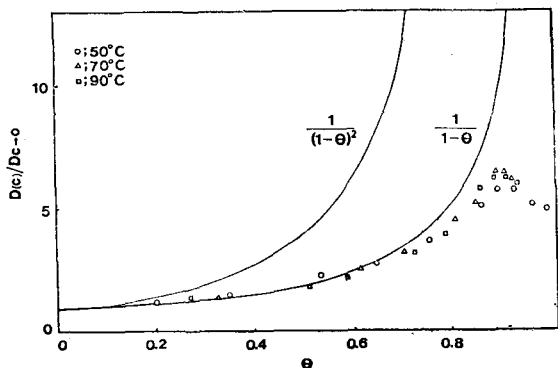


Fig. 19. Test of thermodynamic equations in Dye I.

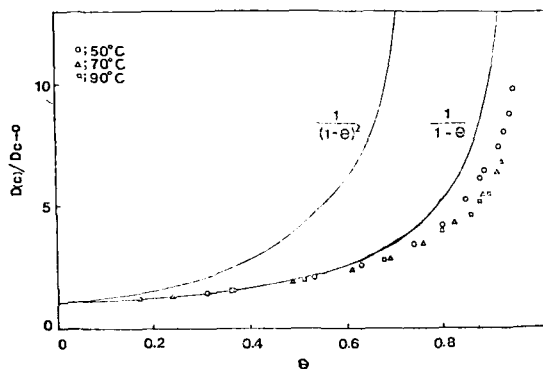


Fig. 20. Test of thermodynamic equations in Dye II.

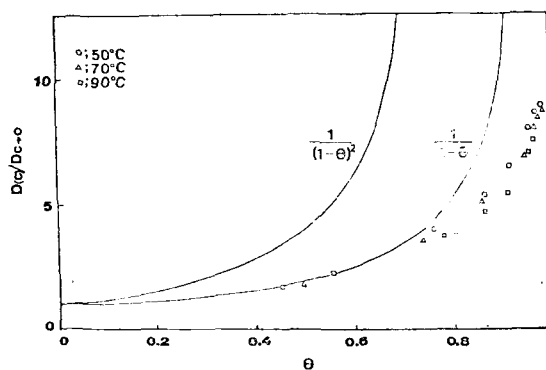


Fig. 21. Test of thermodynamic equations in Dye III.

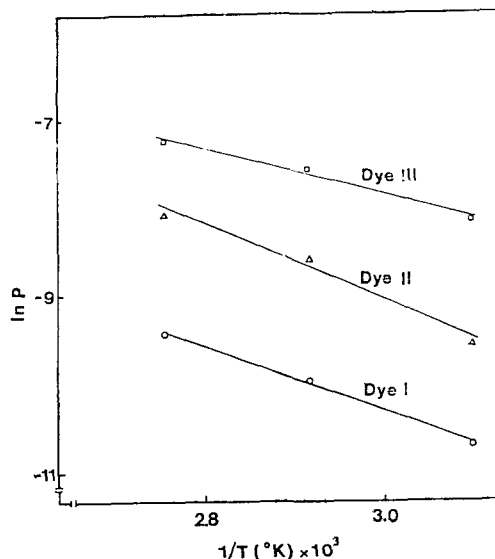


Fig. 22. Arrhenius plots of permeation coefficients of Dye I, II and III.



basicity of dye anion.

On the other hand permeation coefficient can be explained in terms of the activation energy of permeation.

$$\ln \bar{P} = A - E_p/RT \quad (12)$$

Where,  $\bar{P}$  is permeation coefficient,  $E_p$  activation energy of permeation, and  $A$  constant.

The activation energy of permeation may be calculated from the slope of the plot of  $\ln \bar{P}$  against  $1/T$ . Arrhenius plots of permeation coefficients were shown in Fig. 22. The data were summarized in table 2.

It is clearly shown in table 9 that the activation energy of permeation ( $E_p$ ) decreases with the introduction of sulfonic acid group into these dyes. This means that the permeation is more independent on the temperature with the introduction of sulfonic acid group.

Since Dye I has lower solubility than the others, Dye I is to be much more affected by the temperature changes.

**Table 2.** Thermodynamic parameters.

| Dye     | $E_p$ (kcal/mol) |
|---------|------------------|
| Dye I   | 8.64             |
| Dye II  | 8.24             |
| Dye III | 5.46             |

#### IV. Conclusion

Permeation of acid dyes through silk fibroin membrane was measured by the steady-state permeation method and analysed by the dual sorption and diffusion mechanisms.

1) The overall diffusion coefficient  $D_{(C)}$  was largely determined by Langmuir-type diffusion ( $D_L$ ).

2) The diffusion of acid dyes in the silk fibroin becomes slow with the introduction of sulfonic acid groups.

3) On the other hand, the comparison of the  $D_p^0$  values was not very meaningful because of their uncertainties.

4) It was observed that the larger the charge number of the dye anions, the nearer the results

obtained with the theoretical curve given by chemical potential gradient model.

5) The activation energy of permeation decreases with the introduction of sulfonic acid group into these dyes.

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